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Sorption of hexavalent chromium from water and water–organic solvents onto an ion exchanger Tulsion A-23(Gel)

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ABSTRACT

The sorption of hexavalent chromium from water and water–organic solvents onto an ion exchange resin Tulsion A-23(Gel) is reported under various experimental conditions such as initial metal concentration, contact time, temperature, pH, and dielectric constant of the medium. The batch ion-exchange process was relatively fast and it reached equilibrium after 110 min of contact. The ion-exchange process, which is pH dependent, showed maximum removal of chromium(VI) in the pH range 7.0–9.0 for an initial chromium(VI) concentration of 0.0011 M. The equilibrium related to Tulsion A-23(Gel) ion-exchange capacity and the total amounts of the ion exchange were obtained using plots of the Langmuir and Freundlich adsorption isotherms. Various thermodynamic parameters have also been evaluated, including differential adsorption enthalpy and entropy.

Keywords: Chromium(VI); Ion exchange; Adsorption isotherm; Kinetics; Equilibrium

1. Introduction

A large number of metals are employed for various applications in metallurgical, electroplating, leather tanning, metal finishing, chemical industries, mining, etc. These industries release huge amounts of heavy metals such as cadmium, chromium, nickel, zinc, copper, etc., into the natural environment causing not only environmental pollution [1–3] but also adversely affecting aquatic and human life [4]. Among these, Cr(VI) is a highly toxic metal ion even in trace concentration [5,6] and is considered as a priority pollutant released from various chemical industries [7,8]. Cr(VI) can pose health risks such as cancer, liver, kidney, or skin damages, gastrointestinal ulcers [9,10] etc. In 1982 Cr(VI) was considered by the International Agency for Research on Cancer as a powerful carcinogenic agent that modifies the DNA transcription process causing important chromosomic aberrations [11,12]. Cr(VI) is approximately 100 times more toxic than Cr(III) [13]. The United States Environmental Protection Agency drinking water regulations limit the total chromium in

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drinking water to <0.1 mg/L [14]. Also the Ministry of Environment, Government of India, has set minimal national standards of 0.1 mg/L for safe discharge of the effluents containing Cr(VI) into surface waters [15]. Consequently, the removal of Cr(VI) from water and wastewater has gained research interest among the scientific community. Several methods aiming at the removal of chromium have been reported in the literature such as solvent extraction, membrane separation, precipitation, ion exchange, adsorption, reverse osmosis, etc. [16–18]. Among these techniques, ion exchange and adsorption have been shown to be promising and environmentally friendly methods for the removal of heavy metals in solution [19–21].

In the present study, anion exchange resin Tulsion A-23(Gel) was employed effectively for the removal of Cr(VI) ions from water and water–organic solvents at various experimental conditions viz. pH, temperature, period of stirring, effect of organic solvents, and dielectric constant, etc. Kinetic, thermodynamic, and adsorption studies were also carried out. Anion-exchange experiments were made in the presence of organic solvents, 2-methoxyethanol and 2-ethoxyethanol as these solvents are widely used by the industries [22,23]. Tulsion A-23(Gel) is a strong anion-exchange resin with total exchange capacity of 3.2 m eq./g, which offers the possibility of a maximum removal of Cr(VI) in water and water–organic solvent mixed media.

2. Experimental

2.1. Materials

Anion-exchange resin Tulsion A-23(Gel), obtained from Thermax Limited, Pune (India) was used in this study. The typical data of Tulsion A-23(Gel) are summarized in Table 1. The resin was reconditioned by usual method. All other chemicals used were of analytical reagent grade and purchased from Merck chemical company. The solvents 2-methoxyethanol and 2-ethoxyethanol were obtained from Acros organics, USA. Molar solutions of K_2CrO_4 were prepared in water and water–organic solvent mixed media in different proportions ranging from 20% up to 80%.

Table 1
Properties of strong base anion-exchange resin Tulsion A-23(Gel)

Resin	Tulsion A-23(Gel)
Ionic form	Chloride
Resin type	Tough Gel strong base anion
Matrix type	Polystyrene co-polymer
Functional group	Quaternary ammonium type-I
Particle size	0.3–1.2 mm
Moisture	53%
Maximum operating temperature	80℃
pH range	0–14
Total exchange capacity	0.80 m eq./250 g

2.2. Methods

2.2.1. Batch ion-exchange studies

Batch ion-exchange studies were performed by stirring the solutions in presence of a fixed mass of dry resin for a period of 5 h at controlled different temperatures 30, 40, and 50℃ in a Toshiba thermostatic water bath shaker until the equilibrium was reached. At the end of the experiment, the resin was separated by filtration and the supernatant was analyzed for Cr(VI) spectrophotometrically ($\lambda_{\max} = 540$ nm) using the 1,5-diphenylcarbazide method [24]. Equilibrium distribution coefficient (K_d) values were calculated using the Eq. (1) [25]:

$$K_d = \frac{q_e}{C_e} \tag{1}$$

where q_e is the amount of metal ion adsorbed at equilibrium (mol/g) and C_e is the equilibrium concentration of metal ion in solution (mol/L). The Eq. (2) was used to calculate the recovery factor for Cr(VI) from water and water-organic solvent mixed media.

$$\%R = \frac{C_a}{C_o} \times 100 \tag{2}$$

Where C_a is the concentration (mol/L) of Cr(VI) on the resin calculated as the difference between concentrations of Cr(VI) in solution before and after sorption, and C_o is the initial concentration (mol/L) of Cr(VI). From these experiments, the dependence of percentage uptake of Cr(VI) with respect to time was investigated.

2.2.2. Morphology

The sample morphology was observed using a scanning electron microscope (SEM) model JEOL 5400. The specimens for SEM observation were prepared by depositing the fibers onto specimen stubs with conductive double sticky copper tapes, and then sputter-coating (model Polaron SC7640, Quorum Technologies Ltd, UK) the sample surface with Au–Pd to prevent electrical charging during examination. Imaging was done in the high vacuum mode under an accelerating voltage of 10 kV, using secondary electrons.

2.2.3. Fourier transform infrared spectroscopy

The Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer 1720 spectrophotometer in the range of wave numbers 4,000–400 cm^{-1}. Fifty scans were collected at 2 cm^{-1} resolution. The dispersion of the sample with the KBr was placed in a Perkin-Elmer hydraulic press, and a charge of 10 tons was applied for 3 min. A background spectrum was registered previously, using a KBr disk with the same mass and thickness as for the resin sample.

3. Results and discussion

3.1. Characterization of the pristine and Cr(VI)-loaded resin

As indicated in Table 1, Tulsion A-23 is a polystyrene co-polymer resin with quaternary ammonium surface groups. The positive charge of such surface groups is balanced by chloride ions that can be potentially exchanged by Cr(VI) anions (mainly CrO_4^{2-} depending on the pH). Fig. 1 shows the FTIR spectra of the resin registered before (a) and after (b) the adsorption process. The presence of quaternary ammonium surface groups in the raw exchanger is confirmed by the presence of the spectral bands centered at around 920, 970, and 1,480 cm^{-1} [26,27]. The presence of chloride as the counter ion is revealed by the complex group of bands that can be observed in the range comprised between 730 and 850 cm^{-1}. Particularly, the bands centered at 730, 820, and 850 cm^{-1} can be assigned to the C–Cl vibrations [28,29]. An intense band centered at 1,640 cm^{-1} can be observed in the spectrum of the pristine resin. This band is attributable to the presence of C=O bonds in amide groups. Finally, three peaks centered at 2,920, 3,015, and 3,420 cm^{-1} corresponding to –OH, –COOH, and –NH vibrational bands, respectively, can also be identified.

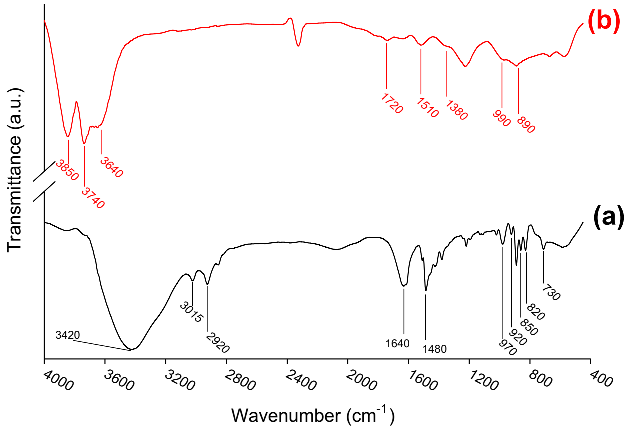
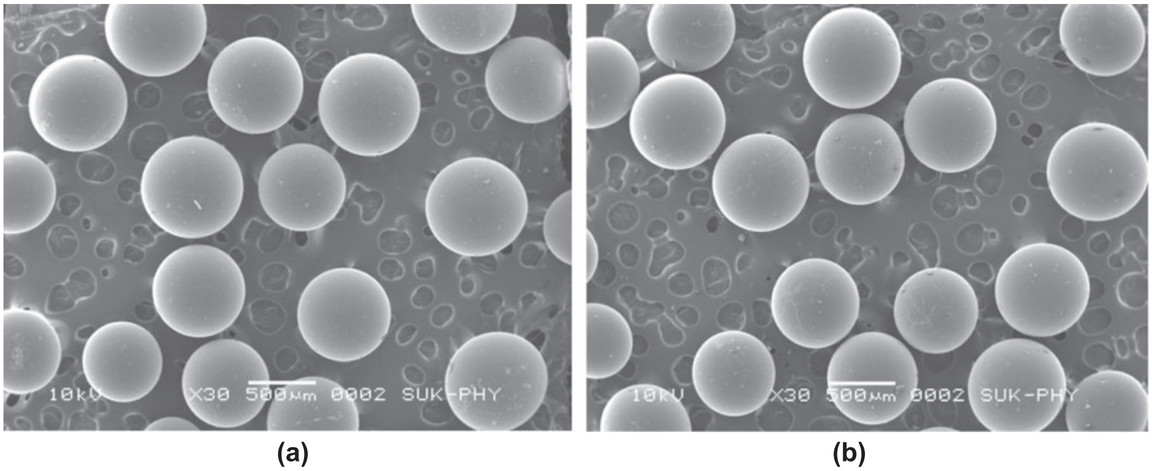


Fig. 1. FTIR spectra of Tulsion A-23 (Gel) (a) before adsorption and (b) after adsorption of Cr(VI).

The FTIR spectrum registered after the adsorption process shows remarkable differences with respect to the original one. Firstly, a band centered at 890 cm^{-1} and a shoulder at 1,380 cm^{-1} reveal the presence of Cr–O and Cr=O bonds, respectively [30]. Hence, it may be affirmed that Cr(VI) is effectively retained by the resin. Furthermore, the band initially centered at 1,480 cm^{-1} (quaternary ammonium) shifts to 1,510 cm^{-1} and decreases noticeably in intensity. The other bands assigned to quaternary ammonium surface groups (namely, those centered around 920 and 970 cm^{-1}) either are absent or appear as a small shoulder around 990 cm^{-1} in the spectrum of the Cr(VI)-loaded sample. This fact clearly indicates that quaternary ammonium surface groups are involved in the retention of the Cr(VI) species. The same applies to the band originally centered 1,640 cm^{-1}, which shifts to 1,720 cm^{-1} with a remarkable decrease in its intensity. This fact indicates that the amide groups also take part in the removal of Cr(VI) species from solution. In addition, the spectral bands assigned to the presence of chloride anions in the original resin disappear after the contact of the resin with the chromate containing solution. This fact corroborates that the retention of chromate species takes place through an ion-exchange process where Cl^{-} ions are substituted by CrO_4^{2-} on the surface of the Tulsion A-23(Gel) resin. Finally, the bands initially centered at 2,920, 3,015, and 3,420 cm^{-1} shift to 3,640, 3,740, and 3,850 cm^{-1}, respectively. These changes in the absorption bands of the FTIR spectrum of the resin after adsorption indicate that –OH, –COOH, and –NH groups also play a vital role in the adsorption of Cr (VI) [31,32].

On the other hand, SEM technique is widely used to study the surface morphology of the adsorbent materials. SEM images of resin Tulsion A-23(Gel) were obtained before and after adsorption of Cr(VI) (Fig. 2). The surface morphology of the resin shows that the pore diameter of the resin was 1–5 μm and this pore size was maintained after the adsorption process. This clearly indicates that the surface morphology was not much affected by the adsorption process.



(a) (b)

Fig. 2. SEM images of Tulsion A-23 (Gel) (a) before adsorption and (b) after adsorption of Cr(VI).

3.2. Effect of the operational parameters on the removal process

3.2.1. Effect of pH and temperature

The pH of the medium is an important variable for the adsorption of Cr(VI) on the ion-exchange resins. The effect of pH on Cr(VI) adsorption by the resin was studied at different pH levels ranging from 4 to 10, keeping other parameters like contact time, temperature, resin dosage, and initial concentration as constant. As seen from Fig. 3, the maximum removal efficiency of Cr(VI) was 96.7% in the pH range of 7.0–9.0 for an initial chromium concentration of 0.0011 M. At higher pH values, the adsorption of Cr(VI) decreases due to the hindrance caused by OH^- ions and negative charge developed on the surface of the resin. At lower pH values, the uptake of Cr(VI) decreases due to the competition between excess of hydrogen ions and Cr(VI) species for adsorption sites [22,33]. In other words, at lower pH values Cr(VI) species forms H_2CrO_4, which is a non-anionic species and therefore does not participate in the anion-exchange process.

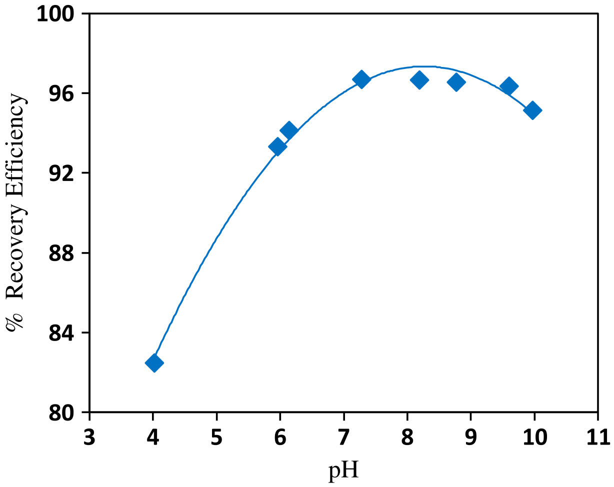


Fig. 3. Effect of pH on chromate removal.

On the other hand, the temperature of the system was varied between 30 and 50˚C. It was observed from Table 2 that with increase in temperature, the level of adsorption decreases due to the decrease in solvation of ionic species in the solution. This indicates the endothermic nature of the process [34]. Thus, the removal of hexavalent chromium decreases as the temperature increases.

3.2.2. Effect of organic solvents and dielectric constant

Experiments were carried out to determine the influence of organic solvents, namely, 2-methoxyethanol and 2-ethoxyethanol on the removal of hexavalent chromium. The calculated distribution coefficient values of ion exchange, K_d, for Cr(VI) on Tulsion A-23 (Gel) in water and water–organic solvent mixed media are listed in Table 2. K_d values vary with organic solvent composition. In fact, the exchange decreases with increase in organic solvent composition from 20 to 80%. As the solvent composition increases, the outside solution becomes less water containing due to the lesser ionization of the inorganic salt in the solution causing a decrease in the exchange of Cr(VI). Also, there will be a continuous decrease in dielectric constant upon addition of 2-methoxyethanol and 2-ethoxyethanol, respectively, to water and hence, the magnitude of distribution coefficient decreases with

Table 2
Distribution co-efficients for chromate on Tulsion A-23(Gel) in water and water-mixed media at different temperatures

	Temperature	Solvent composition in %	Log K_d
2-Methoxy ethanol	30˚C	00	2.4357
		20	2.1418
		40	1.6376
		60	1.5050
		80	1.4455
	40˚C	00	1.8825
		20	1.8305
		40	1.5696
		60	1.3592
		80	1.3490
	50˚C	00	1.8265
		20	1.7941
		40	1.4106
		60	1.2793
		80	1.2621
2-Ethoxy ethanol	30˚C	00	2.4357
		20	2.1069
		40	1.9319
		60	1.6436
		80	1.4109
	40˚C	00	1.8825
		20	1.7491
		40	1.5142
		60	1.4375
		80	1.1162
	50˚C	00	1.8265
		20	1.7445
		40	1.3845
		60	1.2595
		80	1.0473

increase in organic solvent content. Thus, the experimental data support in this context.

3.3. Study of adsorption kinetics

The sorption kinetics explains the uptake of solute which in turn governs the residence time of the sorption reaction. To understand the kinetic aspects of sorption of Cr(VI) on Tulsion A-23(Gel), the sorption study was carried out by batch technique with known mass of resin beads in 30 mL of standard K_2CrO_4 solution in a temperature-controlled water bath shaker. Continuous mixing was provided during the experimental period with constant agitation speed. The remaining concentration of Cr(VI) in each sample, after adsorption at different time intervals, was determined spectrophotometrically. It was seen from Fig. 4 that the extraction of Cr(VI) increased with increasing time of equilibration and decreasing the chromium concentration in solution. The percentage of removal Cr(VI) was increased rapidly up to 110 min and thereafter equilibrium was reached, hence the contact time has not shown much effect in metal removal. Metal removal percentage was fast in the beginning due to the large number of active sites available for the adsorption operations on the resin matrix and then equilibrium was achieved gradually.

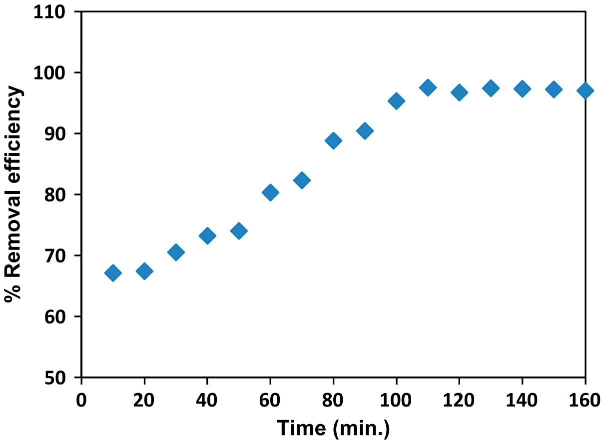


Fig. 4. Effect of interaction time on chromate removal.

The kinetics of hexavalent chromium ion exchange on Tulsion A-23(Gel) obeyed the Lagergren pseudo-first-order rate equation [35] as given below:

$$\log(q_e - q_t) = \log q_e - k\left(\frac{t}{2.303}\right) \tag{3}$$

where q_e and q_t are the amounts of Cr(VI) adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k is the first-order rate constant (min^{-1}) [36]. Using the Eq. (3) and the equation given in Gode and Pehlivan [37] and plotting ln $(1 - U_t)$ vs. time

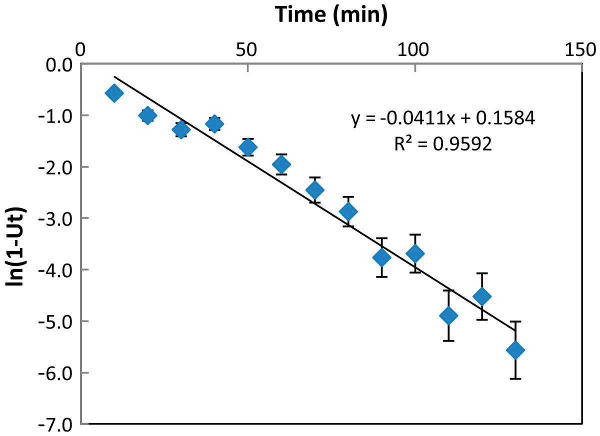


Fig. 5. Kinetic fit for the adsorption of chromium on ion-exchange resin: Tulsion A-23 (Gel).

(Fig. 5) the overall rate constant (0.0411 min^{-1}), forward and backward rate constants, k_1 (0.0402 min^{-1}) and k_2 (0.0009 min^{-1}) were calculated and depicted in Table 3. Where U_t is the ratio of amount of Cr(VI) transferred from liquid phase to solid phase in time t to the concentration of Cr(VI) adsorbed at equilibrium. The forward rate constant was found to be higher than the backward rate constant indicating the dominance of adsorption than desorption. The observed forward rate constant for the removal of Cr(VI) is much higher in case of Tulsion A-23(Gel) compared to Tulsion A-27(MP) resin [22]. This indicates Tulsion A-23(Gel) is better sorbent for the removal of Cr(VI).

3.4. Study of adsorption equilibrium

In order to analyze the equilibrium aspects of the removal process of Cr(VI), three well-known widely used models were applied to the experimental data for comparative purpose.

Such models are those proposed by Freundlich, Langmuir, and Redlich and Peterson. According to the Langmuir adsorption model, the adsorbate molecules are retained in the form of a monolayer onto the sorbent's surface. Such a surface contains a finite number of energetically equivalent active sites and no transmigration of the retained molecules is assumed. On the contrary, the semi-empirical model proposed by Freundlich assumes certain heterogeneity of the surface in terms of the energy of the active sites. This model performs very well at moderate partial pressures or concentrations. However, for dilute vapors or solutions Freundlich's equation is not so useful. On the contrary, at low concentrations Langmuir's equation is extremely useful, albeit its accuracy decreases for moderate or high concentrations. In 1959, O. Redlich and D.L. Peterson proposed an alternative model that showed a wider range of applicability. The results of the fitting of the experimental data to the referred models are provided below.

3.4.1. Freundlich isotherm

The linear form of Freundlich [38] isotherm is represented as,

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log C_e \tag{4}$$

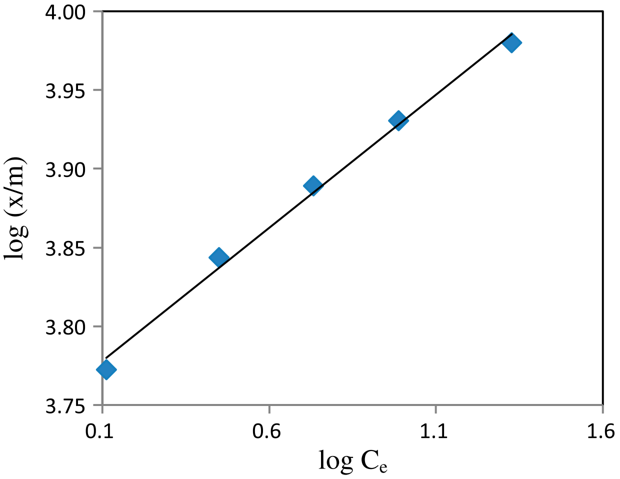


Fig. 6. Freundlich isotherm for the adsorption of chromate on Tulsion A-23 (Gel).

where x/m is the amount of Cr(VI) adsorbed per unit mass of the resin (mg/g), C_e is the equilibrium concentration (mg/L), k is a measure of adsorption capacity and $1/n$ is the adsorption intensity. Plot of log (x/m) vs. log C_e is linear which indicates the use of Freundlich isotherm (Fig. 6). Adsorption is favorable when the value of $1/n$ lies between 0.1 and 1 or the value of n lies between 1 and 10 [39]. The values of constants k and n for the resin Tulsion A-23(Gel) are given in Table 4. Adsorption capacity ($k = 85.57$) for Tulsion A-23(Gel) is higher compared to Tulsion A-27(MP) ($k = 77.74$), Lewatit MP 64 ($k = 83.4$), and Lewatit MP 500 ($k = 13.2$) resins [22,33]. The observed higher values of k and n with Tulsion A-23(Gel) indicate a strong chemical interaction and ion exchange between the resin and Cr(VI).

3.4.2. Langmuir isotherm

Langmuir [40] isotherm model is represented as,

$$\frac{C_e}{q_e} = \frac{1}{K_b}A_s + \frac{C_e}{A_s} \tag{5}$$

where A_s is the ionexchange capacity (mg/g) and K_b (L/mg) is the Langmuir constant related to energy of adsorption and the values are given in Table 4.

Table 3
Rate constants for the removal of Cr(VI) with Tulsion A-23(Gel)

Resin	Cr (VI) amount (mmol)	Overall rate constant, $k = k_1 + k_2$ (min^{-1})	Forward rate constant, k_1 (min^{-1})	Backward rate constant, k_2 (min^{-1})
Tulsion A-23 (Gel)	1	0.0411	0.0402	0.0009

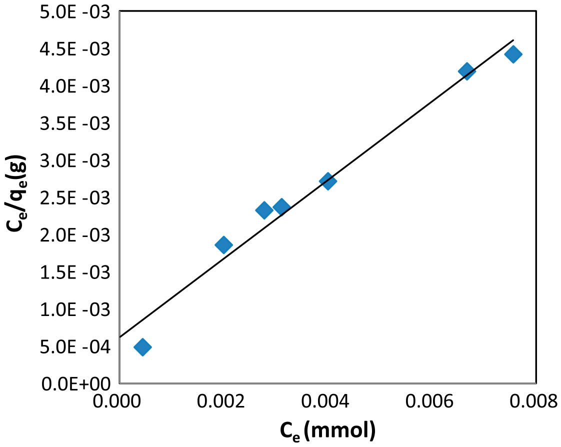


Fig. 7. Langmuir isotherm for the adsorption of chromate on Tulsion A-23 (Gel).

The value of K_b increases with increase in temperature, which confirms that chromate sorption takes place more readily as temperature rises. Langmuir model effectively described the sorption data with r^2 value 0.97 (Fig. 7). The Langmuir model applies to ion exchange on a completely homogeneous surface with negligible interaction between adsorbed molecules.

In order to evaluate the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor or equilibrium parameter, R_L [41] as given in Eq. (6).

$$R_L = \frac{1}{1 + K_b C_o} \tag{6}$$

where K_b is the Langmuir constant and C_o (mg/L) is the initial concentration of Cr(VI). The R_L value between 0 and 1 indicate favorable adsorption for all temperatures studied (Table 4).

3.4.3. Redlich–Peterson isotherm

This is a modified three-parameter isotherm,

$$\ln\left(A\frac{C_e}{q_e} - 1\right) = g \ln C_e + \ln B \tag{7}$$

where A, B, and g represent three isotherm constants and can be evaluated from the linear plot as shown by Eq. (7) using a trial and error optimization method. A general trial and error is used to determine the value of r for a series of values of A for the linear regression of ln $[A(C_e/q_e) - 1]$ vs. ln C_e and to obtain the best value of A which yields a maximum optimized value of r and the respective values of g and B were determined from the slope and intercept of the ln $[A(C_e/q_e) - 1]$ vs. ln C_e. The values are indicated in Table 4.

3.5. Evaluation of thermodynamic parameters

Thermodynamic parameters, namely change in free energy (ΔG), change in enthalpy (ΔH), and change in entropy (ΔS) have been determined for the chromate–chloride exchange as shown in Table 5. Increase in free energy change with increase in percentage of 2-methoxyethanol and 2-ethoxyethanol, respectively, in solution indicates that exchange is facilitated in aqueous and lower solvent composition. The free energy change has negative values and become less negative with increase in percentage of 2-methoxyethanol and 2-ethoxyethanol. Spontaneity of the reaction increases with increase in negative values of ΔG and decreases with increase in organic solvent composition. The negative values of ΔH show exothermic behavior of exchange in aqueous and lower mixed media which supports the decrease in K_d values with rise in temperature. The variation of ΔS along with ΔH, points out that the organic solvent percentage may create a sort of disorder in the water structure so that the entropy changes in aqueous mixed media can be co-related to disorder. The negative values of ΔS indicate the system changes from less orderly state to more orderly state [42].

On the other hand, the use of the Clausius–Clapeyron equations makes it possible to evaluate the evolution of the differential enthalpy (ΔH_{diff}) and entropy (ΔS_{diff}) as the coverage fraction (θ, i.e. the fraction of active sites of the adsorbent that are occupied by adsorbate molecules) increases. Such equations are:

Table 4
Parameters of Freundlich, Langmuir, and Redlich–Peterson isotherms for sorption of Cr(VI) on Tulsion A-23(Gel)

Freundlich isotherm			Langmuir isotherm				Redlich–Peterson isotherm			
k	n	r^2	K_b	A_S[a]	r^2	R_L	A (L/mg)	g	B (L/mg)	r^2
85.57	6.16	0.96	858.93	1.89	0.97	0.514	11.7	0.773	50.67	0.995

[a] mmol/g resin.

$$\Delta H_{\text{diff}} = R \cdot \frac{T_1 \cdot T_2}{T_2 - T_1} \cdot \ln \left(\frac{\frac{C_2}{C_{S_2}}}{\frac{C_1}{C_{S_1}}} \right)_{\theta} \tag{8}$$

and,

$$\Delta S_{\text{diff}} = \frac{R}{T_2 - T_1} \cdot \left(T_1 \cdot \ln \frac{C_1}{C_{S_1}} - T_2 \cdot \ln \frac{C_2}{C_{S_2}} \right)_{\theta} \tag{9}$$

where R is the molar constant of gasses, C_1 and C_2 are the solute concentrations in solution at temperatures T_1 and T_2 respectively, C_{S_1} and C_{S_2} are the solubilities of the solute in the solvent (i.e. pure water or admixtures containing 2-methoxyethanol or 2-ethoxyethanol) at those temperatures and θ is the coverage fraction, i.e. the ratio between the occupied and total active sites of the sorbent's surface.

The application of these equations makes it possible to obtain relevant information regarding the energy distribution of the active sites of the sorbent's surface. If the active sites of the surface are energetically equivalent, then the energy distribution should fit the Maxwell–Boltzmann law. In other words, ΔH_{diff} should be negative along the whole $0 \leq \theta \leq 1$ range, tending to increase from a value of $\Delta H_{\text{diff}} = -\infty$ at $\theta = 0$, up to $\Delta H_{\text{diff}} = 0$ at a value of the coverage fraction, θ, equal to 1.

The values of ΔH_{diff} calculated from the experimental data have been plotted in Fig. 8. This figure includes the ΔH_{diff} vs. θ plot corresponding to the experiment performed using pure water as the solvent, as well as those corresponding to the different 2-methoyethanol:water (a) and 2-ethoxyethanol:water (b) admixtures. For those experiments performed in pure water, the shape of the ΔH_{diff} vs. θ plot follows the trend predicted by the Maxwell–Boltzmann law up to a value of coverage fraction approximately equal to 0.2. For larger values of θ, however, ΔH_{diff} tends to decrease probably due to the occurrence of side interactions between the adsorbed molecules of the adsorbate. The same applies for the admixtures containing 20 and 40% of 2-methoyethanol. Nevertheless, a final increasing portion may be observed when pure water is used. This increase, which can be assigned to the presence of a more remarkable affinity of the active sites of the adsorbent towards the solvent, does not occur when 2-methoyethanol is present in the system even at relatively low concentration. The most remarkable feature in these ΔH_{diff} vs. θ plots is the delay in the adsorption process that may be appreciated when the concentration of 2-methoyethanol increases. This fact is attributable to an initial the inactivation of the surface sites by preferential and strong adsorption of solvent molecules. As a consequence, at the initial stages of the adsorptive process, the solute molecules are only accessible to a relatively reduced number of high-energy surface sites of the sorbent.

On the other hand, for the adsorption experiments performed using water: 2-ethoxyethanol admixtures the ΔH_{diff} vs. θ plots fit relatively well to the Maxwell–Boltzmann law, particularly for a water: 2-ethoxyethanol ratio equal to 80:20. Hence, the active sites of the adsorbent's surface can be regarded as energetically equivalent for the adsorption of chromate from the water: 2-ethoxyethanol admixture. For larger 2-ethoxyethanol proportions a slightly decreasing portion can be observed in the plots. As indicated above,

Table 5
Thermodynamic parameters for exchange of chromate anion against chloride of the resin phase in water-mixed media at different temperatures

	ΔG (kJ mol^{-1})			ΔH (kJ mol^{-1})		ΔS (J K^{-1} mol^{-1})	
	303 K	313 K	323 K	303–313 K	313–323 K	303–313 K	313–323 K
2-Methoxy ethanol (%, v/v)							
00	−14.1	−11.3	−11.3	−100.5	−10.8	−284.9	1.4
20	−12.4	−11.0	−11.1	−56.5	−7.0	−145.6	12.5
40	−9.5	−9.4	−8.7	−12.3	−30.8	−9.4	−68.3
60	−8.7	−8.1	−7.9	−26.5	−15.5	−58.6	−23.4
80	−8.4	−8.0	−7.8	−17.5	−16.8	−30.2	−27.9
2-Ethoxy ethanol (%, v/v)							
00	−14.1	−11.3	−11.3	−100.5	−10.8	−284.9	1.4
20	−12.2	−10.5	−10.8	−65.0	−0.9	−174.1	30.6
40	−11.2	−9.1	−8.6	−75.8	−25.1	−213.3	−51.2
60	−9.5	−8.6	−7.8	−37.4	−34.5	−92.1	−82.6
80	−8.2	−6.7	−6.5	−53.5	−13.3	−149.6	−21.2

Note: Error ± 5%.

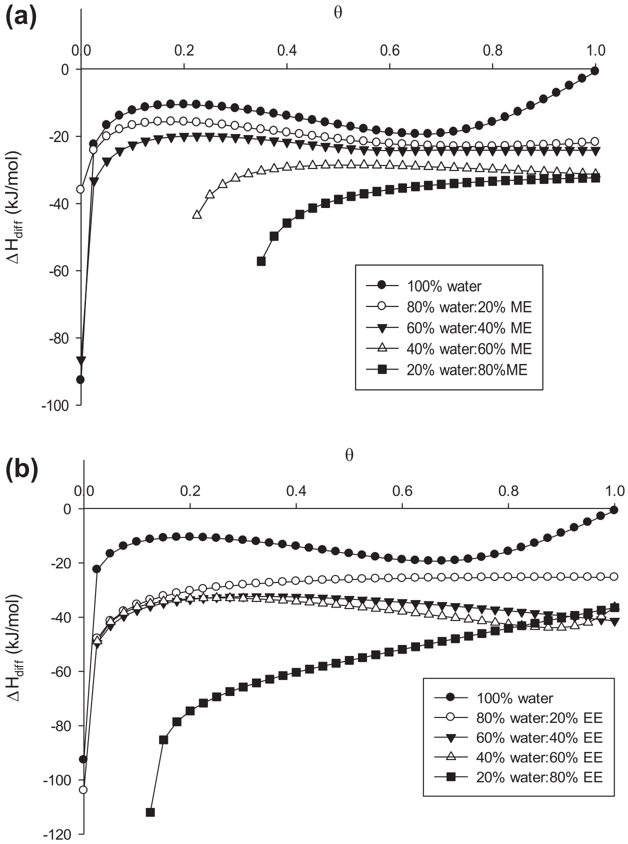


Fig. 8. Variation in differential adsorption enthalpy with coverage fraction calculated from the adsorption isotherms of Cr(VI) in water and 2-methoxyethanol (a) or 2-ethoxyethanol (b).

this is indicative of the occurrence of side interactions between the adsorbed molecules of the adsorbate. Finally, the steadily increasing shape of the plot corresponding to 80% 2-ethoxyethanol suggests that the affinity of the active sites towards the solvent is remarkably higher than in the remaining cases.

The ΔS_{diff} vs. θ plots (not shown for the sake of brevity) reveal that ΔS_{diff} is positive along the whole interval of coverage fraction, θ. This fact suggests that the retention of the Cr(VI) species initially present in solution takes part with a remarkable degree of desolvation of the active sites as a previous stage of the adsorption/ion-exchange process. This is in accordance with all the above exposed. Finally, it is worth noting that, as usual, the shape of the ΔS_{diff} vs. θ plots is opposite to that of the ΔH_{diff} vs. θ plots.

4. Conclusion

Ion-exchange resins have been considered as efficient materials for the treatment of contaminated water with selected heavy metals. Equilibrium studies of removal of hexavalent chromium by anion-exchange resin Tulsion A-23(Gel) followed Freundlich, Langmuir, and Linear adsorption isotherms. The values of adsorption capacity and intensity of adsorption indicate the higher affinity of the resin towards the chromium. The adsorption of Cr(VI) increased with agitation period and attained an optimum at about 110 min. The maximum removal (96.87%) of Cr(VI) by the resin was at an optimum pH between 7.0 and 9.0. The promising results obtained during the batch experiments revealed that the method was technically feasible and the resin Tulsion A-23(Gel) was efficient in the removal of Cr (VI) from aqueous and mixed-aqueous solvents. Thus, the anion-exchange resin Tulsion A-23(Gel) can be an attractive sorbent for the treatment of water and wastewater containing traces of Cr(VI) ions in the appropriate pH range.

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